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Controlling the Color of Cholesteric Liquid-Crystalline Films by Photoirradiation of a Chiroptical Molecular Switch Used as Dopant**

By Richard A. van Delden, Marc B. van Gelder, Nina P. M. Huck, and Ben L. Feringa*

Using thin films of a cholesteric mixture of acrylates **2** and **3** doped with the chiroptical molecular switch (*M*)-*trans*-**1**, photocontrol of the reflection color between red and green is possible. This doped liquid-crystal (LC) film can be used for photoinduced writing, color reading, and photoinduced locking (via polymerization) of chiral, optically written information.

1. Introduction

The prospects of nanotechnology offer a tremendous challenge in the development of new materials and devices.^[1] In the bottom-up approach towards miniaturized devices, considerable progress has been made in the realization of several functions controlled at the molecular level. For instance, molecular switches,^[2] brakes,^[3] muscles,^[4] turnstiles,^[5] and motors^[6] have been reported. The so-called *nanoassembly* of a number of these functional molecules has been accomplished by elegant and versatile organic synthesis and supramolecular approaches.^[7] The functioning of these systems has been demonstrated by sophisticated measurements, although almost exclusively in solution experiments. The next step would be to actually find a practical use in real nanotechnological applications.^[8] An important aspect of the research efforts towards this goal is to amplify the molecular function to a macroscopic change in the properties of a material. Liquid crystals (LCs) constitute very promising host materials for this type of molecular devices, since LC materials are known to be sensitive to small (molecular) perturbations resulting in a macroscopic change of the systems.^[9] Here, the use of LCs to amplify the molecular chirality of a chiroptical molecular switch^[2] is presented. Furthermore, it is demonstrated that a color change of a LC film can be induced by photoisomerization of a chiral dopant. It is shown that the colored doped LC film can be used for photoinduced writing, color reading, and photoinduced locking of chiral–optically written information.

LCs are widely applied in display technology.^[10] These liquid-crystal displays (LCDs) make use of the so-called electro-optical response of a LC material. Color is generally induced by color filters in combination with electronically addressable

bright or dark sub-pixels.^[11] A colored LC matrix addressable by light could offer a useful alternative, considering the speed of addressing or the resolution of pixel sizes for a photo-addressable LCD are limited only by the dimensions of light. Cholesteric LCs are especially promising materials for these applications, as LC materials with photocontrollable pitches in the range of visible light offer the advantage of direct color control. Cholesteric LC can be induced by doping achiral–nematic LC with chiral dopants. Cholesteric phases are assigned by a helical packing of the mesogens with a certain sign and a certain pitch.^[12] The pitch, the distance in a LC needed for the director of the individual mesogens to rotate through a full 360°, is a measure of the chirality of the system. These cholesteric phases, when illuminated with white light, reflect light of a certain wavelength dependent on the pitch of the LC phase. The reflection observed is a Bragg-type reflection caused by the repetition of the helical packing.^[13] The wavelength of the most important perpendicular reflection (λ) is given by Equation 1.

$$\lambda_{\perp} = n \times p \quad (1)$$

In this equation, n is the average refractive index of the LC sample and p is the cholesteric pitch. Control of the color of a cholesteric phase has been shown to be possible by light.^[14] The combination of these cholesteric phases with photoswitchable compounds might lead to an all-optical LC display. An early example of reversible LC color changes employed the photoisomerization of an azobenzene in a cholesteric mixture of cholesteryl nonanoate and cholesteryl chloride.^[15] Most of the literature examples are based on cholesteric polymers^[14] and a large variety of copolymers with liquid-crystalline properties and switching units, mainly menthone-based switches^[16,17] or binaphthyl switches,^[18] have been described. Recently, a polymeric LC system was reported where switching an azobenzene dopant was accompanied by crosslinking of the polymeric LC due to the presence of a diacrylate and a polymerization initiator.^[19] This resulted in simultaneous switching and crosslinking from a polymeric LC state showing an approximately 645 nm reflection, to a crosslinked state maximally showing an approximately 750 nm reflection. In an approach comparable to our approach reported in this article, the authors make elegant use of the simultaneously occurring

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light-induced switching and crosslinking, but only red colored liquid-crystalline and crosslinked samples were obtained. There are only a few examples of low molecular weight cholesteric liquid crystals for which the reflection color could be controlled by photoirradiation, and all of these examples are based on the photochromism of an azobenzene dopant.^[20] A prominent example, beyond the azobenzene-doped systems, that was recently reported comprises the color control of a LC phase doped with a unidirectional molecular motor.^[21] In case of the chiroptical molecular switches^[2] it was shown that the handedness of a cholesteric phase could be reversibly inverted upon irradiation with light of a suitable wavelength, although the helical twisting powers were too low to reach colored LC phases.^[22] The amplification of the chiral properties of these molecular components is, however, considered essential for the further developments of photocontrolled materials and devices in, for example, optical data storage and optical data processing. The pitch of these cholesteric phases can be tuned by photochemical control of the chiral properties of the dopants resulting in a macroscopic response. Here we report the possibility of color tuning of a photopolymerizable LC film using a chiroptical molecular switch.

2. Results and Discussion

Our chiroptical molecular switches are based on sterically overcrowded alkenes functionalized with both an electron-withdrawing (nitro) and an electron-donating (dialkylamine) substituent, as illustrated for compound **1** in Figure 1.^[23] This asymmetric substitution of the lower half of the molecule allows selective switching between the *cis*- and the *trans*-isomer. These two isomers are pseudoenantiomers due to their opposite helicity; *M*-helicity in the case of the depicted *trans*-**1** and *P*-helicity in case *cis*-**1**, as reflected in their circular dichroism (CD) curves (Fig. 2A).^[24] The *N*-alkyl-sub-

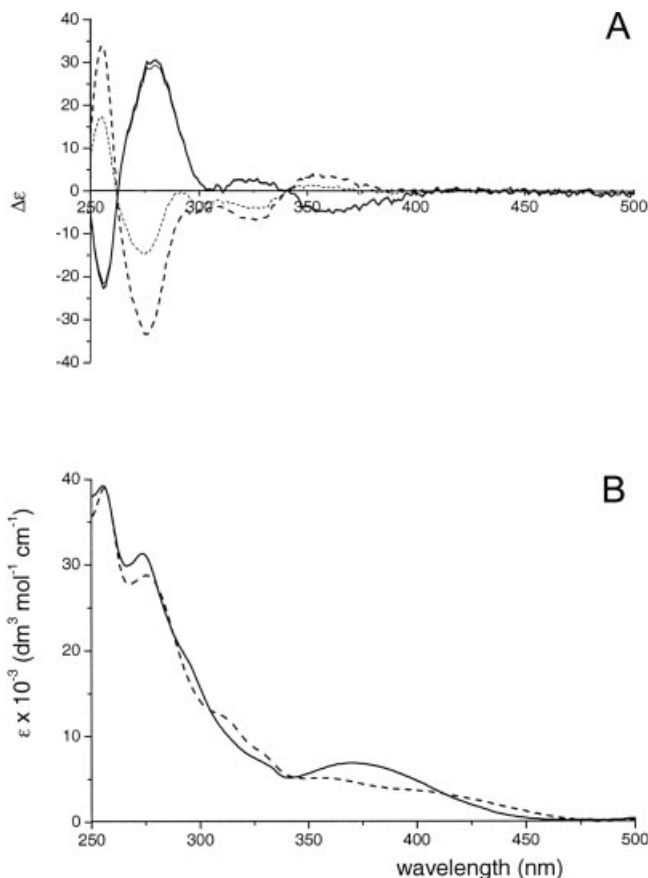


Fig. 2. CD (A) and UV-vis spectra (B) of (*M*)-*trans*-**1** and (*P*)-*cis*-**1**. The dashed curves correspond to (*M*)-*trans*-**1** and the solid curves correspond to (*P*)-*cis*-**1**. Also depicted (A) are the CD spectra obtained for the two photostationary states 465 nm (thin solid curve) and 380 nm (thin dashed curve).

stituents are introduced to enhance compatibility with the LC matrix.

The interest in colored cholesteric phases based on LC materials doped with chiroptical molecular switches is twofold.

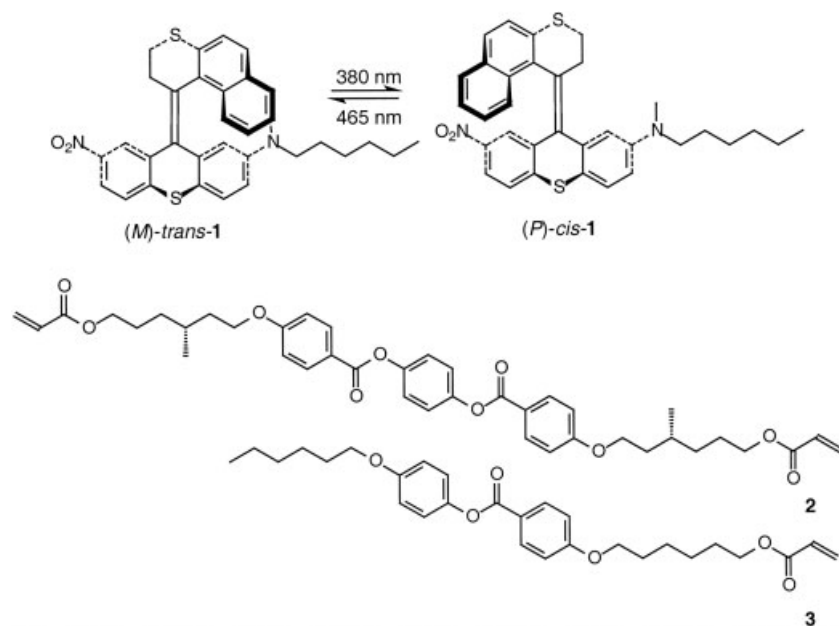


Fig. 1. Structures of the chiroptical molecular switch **1** and monomeric acrylates **2** and **3** (for the photopolymerizable cholesteric mixture).

When chiroptical molecular switches can induce pitch lengths in the range of the dimensions of the wavelength of visible light, a direct color read-out of written information is possible. On the other hand, as noted, direct color tuning of the cholesteric phase opens up the opportunity to develop color liquid-crystal displays addressable by light. The two pseudoenantiomers show near mirror image CD spectra in *n*-hexane solution and also near mirror image behavior in liquid-crystalline matrices where the two pseudoenantiomers have opposite helical twisting powers (HTP). In the commercially available nematic LC host E7 (which is liquid crystalline at room temperature), for example, helical twisting powers of $-13.5\ \mu\text{m}^{-1}$ and $+10.1\ \mu\text{m}^{-1}$ were determined for (*M*)-*trans*-**1** and (*P*)-*cis*-**1**, respectively. In *n*-hexane solution, driven by a distinct difference in UV-vis absorption, the system can reversibly be switched from a photostationary state with 70 % (*M*)-*trans*-**1** and 30 % (*P*)-*cis*-**1** by employing 380 nm light and a photostationary state with 2 % (*M*)-*trans*-**1** and 98 % (*P*)-*cis*-**1** employing 465 nm light. These photostationary states of opposite chirality (Fig. 2A) are thermally stable under ambient conditions. The difference in UV-vis absorption for the two forms (*M*)-*trans*-**1** and (*P*)-*cis*-**1** is the driving force for switching (Fig. 2B). Details of the synthesis, spectroscopic data, and thermal and photochemical isomerization of **1** in solution will be reported elsewhere.

The switching ability is retained in a LC environment, although the isomer ratios in the photostationary states change slightly. In E7, 380 nm irradiation of a film doped with 2.6 wt.-% of enantiomerically pure (*M*)-*trans*-**1** resulted in a photostationary state consisting of 77 % (*M*)-*trans*-**1** and 23 % (*P*)-*cis*-**1**, whereas 470 nm irradiation resulted in a second photostationary state consisting of 13 % (*M*)-*trans*-**1** and 87 % (*P*)-*cis*-**1** (as determined by chiral high performance liquid chromatography (HPLC)). For this system, full switching of the sign of a cholesteric phase is possible. At 2.6 wt.-% of **1** doped in E7, 380 nm and 470 nm irradiation result in reversible switching between cholesteric phases with a pitch of -5.1 and $+5.5\ \mu\text{m}$. By varying the wavelength of irradiation, cholesteric phases with intermediate pitches can be induced. Employing nematic LC hosts such as E7, minimally pitches in the micrometer range can be obtained, where for any color LCD application pitches in the nanometer range are required. A possible way to achieve these small pitch dimensions is by employing a cholesteric host material. An important advantage of using a cholesteric host is that, upon doping with a chiroptical switch, the color of the LC phase only has to be influenced rather than fully induced.

For two important reasons, the system of choice was a chiral polymerizable cholesteric acrylate mixture (compounds **2** and **3**) developed by Philips Research (Fig. 1).^[25] First, as a result of the chirality of the diacrylate, the host LC phase is already cholesteric. Second, due to the presence of both an achiral monoacrylate and a diacrylate, this system has the possibility to undergo photopolymerization when a suitable photoinitiator is present. The copolymerization locks the cholesteric helix to generate a stable polymeric matrix with optical properties resembling those of the initial LC matrix. This approach allows stable storage of information and color. The exact properties are de-

pendent on the ratio of the two components. For the present research, a mixture of 40 % chiral (*S,S*)-diacrylate **2** and 60 % achiral monoacrylate **3** was used. This mixture forms a cholesteric phase with a maximum reflection wavelength of about 440 nm. Upon polymerization the material shrinks slightly, thereby decreasing the reflection wavelength by 5–15 nm, depending on the amount of polymerization inhibitor used.

A sample of 2.6 wt.-% of a racemic *cis*-*trans* mixture of **1** was tested. Doping of a LC mixture of 40 % **2** and 60 % **3** (forthwith denoted as **2/3**) with the racemic *cis*-*trans* mixture of **1** resulted in a large decrease in the solid (C) to cholesteric (N*) phase transition temperature from 57 °C to 40 °C. This decrease in temperature was more pronounced for samples of higher dopant concentration. Doped samples with 10 and 12.5 wt.-% of enantiomerically pure (*M*)-*trans*-**1** resulted in liquid crystallinity at room temperature. This is a very desirable feature since for any LCD application, liquid crystallinity at room temperature is an absolute requirement. The switching selectivity for **1** was tested on samples of **2/3** doped with 2.6 wt.-% of a racemic mixture of *cis*- and *trans*-isomers of **1**. The switching selectivities in this cholesteric host are lower than the selectivities found in *n*-hexane solution, but clearly show that switching is readily achieved in such a restricted environment. Upon 435 nm irradiation, a photostationary state was reached with a *cis*-/*trans*-**1** ratio of 67:33. Irradiation at 380 nm resulted in a photostationary state of 31 % *cis*-**1** and 69 % *trans*-**1**. The dependence of the wavelength on the switching selectivity was not further investigated.

In order to photomanipulate the color of the LC phase, samples were prepared with increasing doping levels of enantiomerically pure (*M*)-*trans*-**1** dopant (5–20 wt.-%). Stable samples were obtained with up to 15 wt.-% dopant concentration. The transmission characteristics of these samples were measured on aligned and spin-coated samples. In all doped samples, the reflection wavelength was red-shifted compared to the undoped mixture. The red-shift increases with increasing concentration up to 12.5 wt.-%, as depicted in Figure 3. For the 15 wt.-% sample, the observed reflection wavelength was found to have blue-shifted by 49 nm relative to the 12.5 wt.-% sample, indicating some instability at this higher concentration. This might be caused by phase separation but this was not visually detected.

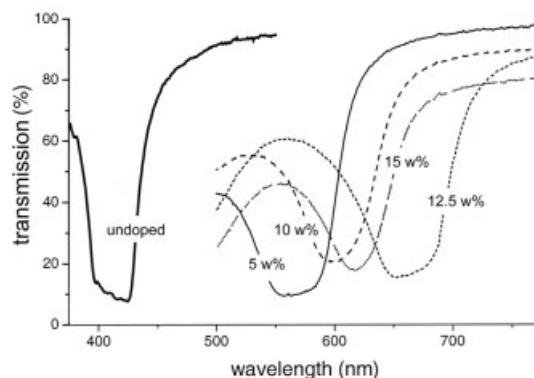


Fig. 3. Influence of dopant **1** concentration on the reflection, wavelength and intensity of aligned and spin-coated cholesteric films.

The influence of photoisomerization of the dopant on the reflection wavelength of the LC film was tested on all the samples differing in dopant concentration (the results are summarized in Table 1). The effect of the photoisomerization on the reflection wavelength increases with increasing dopant concen-

Table 1. Influence of irradiation (photoisomerization and subsequent photopolymerization) on the reflection wavelength of the cholesteric LC phase (2/3).

(<i>M</i>)- <i>trans</i> -1 doping level [wt.-%]	$\lambda_{\text{reflection}}$	$\lambda_{\text{reflection}}$ PSS 435 nm	$\lambda_{\text{reflection}}$ PSS 450 nm	$\lambda_{\text{reflection}}$ after photopolymerization at 365 nm
5	564 nm	536 nm	–	618 nm
10	598 nm	536 nm	–	538 nm
12.5	666 nm	541 nm	526 nm	518 nm
15	617 nm	–	–	–

tration as could be anticipated. Time-dependent switching experiments were performed on an aligned sample with 10 wt.-% (*M*)-*trans*-1 dopant in the presence of 1 wt.-% of photoinitiator (Irgacure 651) and 1 wt.-% of inhibitor (*p*-methoxyphenol) upon 435 nm irradiation. At this wavelength, which is outside the absorption range of the photoinitiator, no polymerization is initiated and a *trans*- to *cis*-isomerization of the chiral dopant is the only process observed. Upon photoisomerization, the reflection band of the LC film was gradually shifted to shorter wavelength (Fig. 4). Starting at a reflection wavelength of 598 nm, a blue-shift of the reflection wavelength to 536 nm was observed in the photostationary state after 150 s of irradiation.

Of all the tested samples, for the 12.5 wt.-% sample the wavelength shift upon photoisomerization at 435 nm was most pronounced. Starting at a reflection wavelength of 666 nm, under irradiation at 435 nm a photostationary state was reached with a reflection wavelength of 541 nm. This represents a blue shift of 125 nm (Fig. 5). However, the irradiation wavelength of 435 nm is not the most efficient switching wavelength for compound 1. When increasing the irradiation wavelength using a 450 nm cut-off filter, the wavelength of reflection could be further decreased to a value of 526 nm. This blue-shift of 140 nm can also be induced directly by irradiation at > 450 nm of the initial pure (*M*)-*trans*-1 doped film.

For the different samples, subsequent photopolymerization of the LC film at the photostationary state was affected by 5 min irradiation at 365 nm in vacuo. A schematic representation of all the processes involved is depicted in Figure 6. At this wavelength *cis* to *trans* back isomerization is expected to occur to some extent. After the irradiation, a polymerized rigid LC phase was obtained. The influence of the photopolymerization on the observed reflection wavelengths is complicated due to the simultaneous occurrence of two processes, photoisomerization and photopolymerization, each affecting the packing of the mesogens. At low concentration (5 wt.-%)

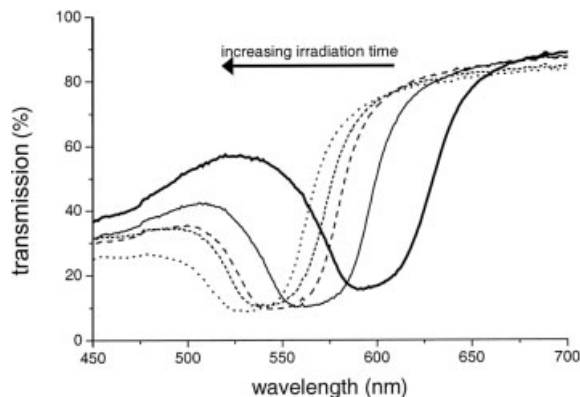


Fig. 4. Color tuning by photoisomerization at 435 nm of 10 wt.-% of switchable dopant (*M*)-*trans*-1 in cholesteric host material 2/3; decreasing line thickness indicates increasing irradiation time ($t = 0, 30, 60, 90, 120$, and 150 s).

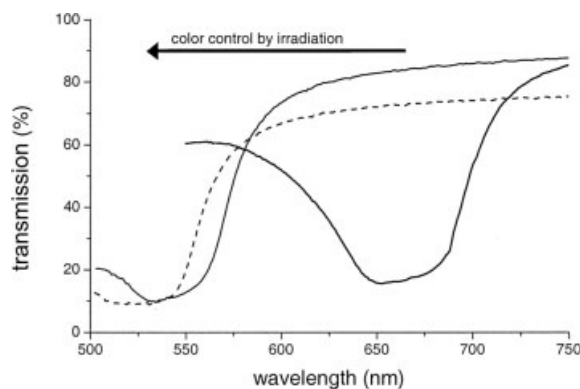


Fig. 5. Change in reflection wavelength by photoisomerization at 435 nm (thin solid line) and subsequently 450 nm (dashed line) of 12.5 wt.-% of a thin LC film of switchable dopant 1 in cholesteric host material 2/3 in its photostationary states.

photopolymerization resulted in a red-shift of the reflection band, as is also observed for the parent compound. The more concentrated samples of 10 and 12.5 wt.-% did not show this effect. At 10 wt.-% the cholesteric packing was apparently unaffected by the photopolymerization, while at 12.5 wt.-% a slight blue-shift accompanied by a broadening effect, was observed (Table 1).

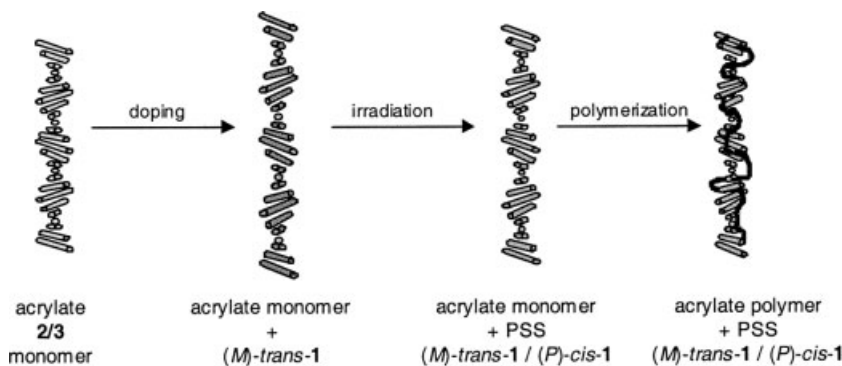


Fig. 6. Schematic representation of processes involved in LC films of cholesteric acrylate mixture 2/3 doped with chiroptical molecular switch 1.

For the 12.5 wt.-% sample, which is most promising for any color LC application due to the largest changes achieved, the effect of the photopolymerization was also tested for the initial, enantiomerically pure (*M*)-*trans*-**1** doped phase showing a 666 nm reflection in the monomeric state. Here, photopolymerization at 365 nm changed the reflection wavelength to 632 nm (Fig. 7A–C), which can be explained by shrinkage of the material. This is also observed for undoped samples and

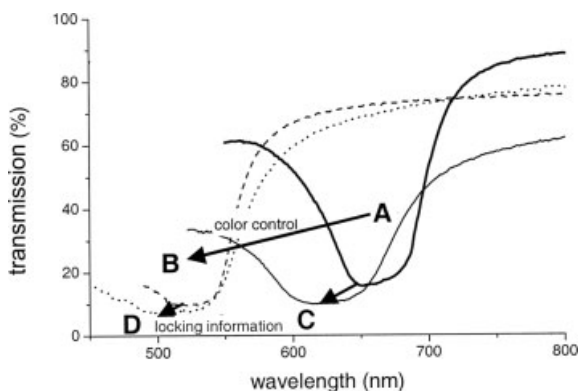


Fig. 7. Color control to write information and photopolymerization as a locking mechanism for a 12.5 wt.-% sample of (*M*)-*trans*-**1** in **2/3**. Wavelength of reflection at different stages of the process: A) initial sample; B) photostationary state after 450 nm irradiation; C) polymerized sample after 365 nm irradiation of the initial sample (A); D) polymerized sample after 365 nm irradiation of the photostationary state (B).

caused by the fact that the polymer is of smaller dimensions than the monomer mixture. The photostationary mixture showed a reflection of 526 nm (Fig. 7B) and gave a polymerized matrix with a 518 nm reflection (Fig. 7D). These results show that the obtained polymeric phases in all cases reflect the photostationary state of the chiral dopant, although there is a small, yet undetermined, degree of *cis*- to *trans*-isomerization during the photopolymerization process.

This system constitutes a “write and lock” mechanism for color information. The polymerized phases are completely inert to prolonged irradiation and the photochemically written color information is locked.

As schematically shown in Figure 8, starting from 12.5 wt.-% (*M*)-*trans*-**1** in acrylate mixture **2/3**, writing is achieved by irra-

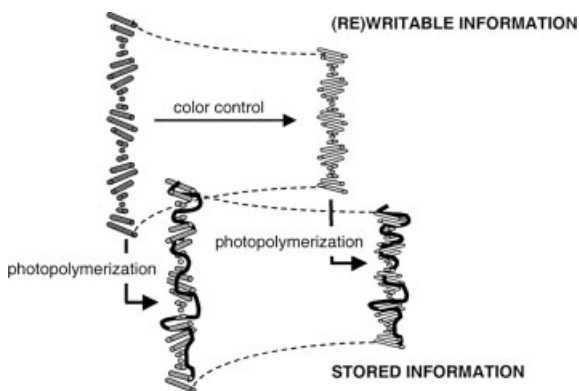


Fig. 8. Schematic representation of color control and storage of information by photopolymerization of a cholesteric LC.

diation with 450 nm light, and cholesteric phases with pitches between 666 nm (initial state) and 526 nm (photostationary state) can be induced by varying the irradiation time. Color inspection (red to green) offers an easy read-out procedure. Further irradiation will result in a change in the (*M*)-*trans*-**1** to (*P*)-*cis*-**1** ratio and consequent change in the wavelength of reflection (the color) of the LC film, as long as the 450 nm photostationary state is not reached. This monomeric state can be considered a rewritable state. Upon photopolymerization the LC matrix will harden and the written information is locked. The polymerization process is accompanied by a slight change in the (chiral) properties of the LC phase. Polymerized cholesteric film with pitches between 632 and 518 nm can be obtained, dependent on the (*M*)-*trans*-**1**/(*P*)-*cis*-**1** ratio before photopolymerization. Again, color inspection (orange to green) offers an easy read-out procedure, which is now absolutely non-destructive. The information is locked and there is no change in cholesteric pitch observed upon further irradiation.

3. Conclusion

In summary, with an aligned and spin coated sample of 12.5 wt.-% (*M*)-*trans*-**1** doped in a cholesteric mixture of acrylates **2** and **3** (40:60), photocontrol of the reflection color of the film between red and green is possible in only about three minutes. By varying time and wavelength of irradiation, all cholesteric phases with intermediate pitches can be reached. The written color information can be stored by subsequent photopolymerization. This wavelength range covers about one third of the whole visible wavelength spectrum, and as such for a real LCD application the system has to be further improved. Nevertheless, the presented system shows a successful use of chiral molecular switches in LC materials in an approach towards real devices. The change in chiroptical properties of a dopant molecular switch results in a visually detectable change in the macroscopic properties of a colored LC host material. The molecular function is amplified to a macroscopic response and as such the cholesteric host offers a macroscopic window into the nanoworld.

4. Experimental

Materials: The synthesis and resolution of chiroptical molecular switch **1** will be reported elsewhere. The cholesteric mixture of **2** and **3**, as well as the photoinitiator (Irgacure 651) and inhibitor (*p*-methoxyphenol), were kindly provided by Philips Research and were used without prior purification.

LC Films: Colored LC films were obtained by alignment of a cholesteric LC material on a polyimide-covered glass surface. For this purpose a glass surface (typically 6.25 cm²) was carefully cleaned with aqueous detergent and with organic solvent (2-propanol). This clean and dry surface was spin coated (at approximately 3000 rpm for 1 min) with commercially available polyimide AL1051 (purchased from JSR, Belgium). These coated glass surfaces were allowed to harden at 170 °C in vacuo for 3 h. The surface was then linearly rubbed with a velvet cloth to induce a parallel-aligned pattern, which could be detected visually and is necessary to induce a plane-parallel alignment of the cholesteric LC phase. The LC material doped with the appropriate amount of dopant dissolved in toluene or dichloromethane (±5 mg mL⁻¹) was slowly poured onto this alignment layer. After evaporation of the solvent at elevated temperature (about 40 °C) the

LC samples were spin coated at 5 rpm for 2 min, resulting in thin LC films with homogeneous colors. All experiments were performed at Philips Research, Eindhoven.

Reflection Wavelengths: The reflection wavelengths presented were measured using a Perkin Elmer Lambda 900 UV-vis-NIR spectrometer. The incident light beam travels through a depolarizer and a polarizer before it reaches the sample. After the sample the transmitted light travels through a $\lambda/4$ plate to isolate the circularly polarized components and a second polarizer before being analyzed.

Irradiation Experiments: Irradiations were performed with a UV lamp equipped with a suitable interference filter (435 nm) or cut-off filter (>450 nm). For the photopolymerization a 365 nm light source was used (Philips PL10W/10). For the initial photoswitching in E7, irradiations were performed with a 150 W Oriel Xe-lamp attached to an Oriel Monochromator. The exact intensity of the light is unknown, but the intensity was constant during all the irradiation experiments reported here. Photostationary states ratios were analyzed by HPLC analysis using a Chiralcel OD column (5 μ m; 250 \times 4.6 mm) with *n*-heptane/2-propanol (90:10) as an eluent and detection at an isosbestic point by a 996 Photodiode Array Detector. Elution times were: (*M*)-*trans*-1: 7.88 min, (*P*)-*cis*-1: 6.10 min.

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